Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

STUDIES INTO THE THERMAL STABILITY AND REACTIVITY OF AMMONIUM NITRATE
PART 2: SOLID STATE DECOMPOSITION OF AMMONIUM NITRATE

P.P. Lee, K. Ketcheson and R.R. Vandebeek

CANADIAN EXPLOSIVES RESEARCH LABORATORY

March 1986

This document is an unedited interim report prepared primarily for [illegible] and external exploitation purposes. It does not represent a final expression of the opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

Ce document est un rapport provisoire non-révisé et rédigé principalement pour fin de diffusion et de documentation interne. Il ne représente nullement l'expression définitive de l'opinion du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

MICROMEDIA

AUG 19 1986

ADMINISTRATION OF THE CANADA EXPLOSIVES ACT
MINING RESEARCH LABORATORIES
DIVISION REPORT ACEA/MRL 86-21(TR)

STUDIES INTO THE THERMAL STABILITY AND REACTIVITY OF AMMONIUM NITRATE
PART 2: SOLID STATE DECOMPOSITION OF AMMONIUM NITRATE

by

P.P. Lee*, K. Ketcheson** and R.R. Vandebeek***

ABSTRACT

Thermal decomposition of ammonium nitrate (AN) below its melting point was studied using two different systems at isothermal temperatures of 120°C, 140°C and 160°C. The static system was a confined environment and the results of percent weight loss, nitric acid content and nitrous fumes increased with increasing temperature. A dynamic system, a flow through system, was used to determine the gas evolution during decomposition. The concentration of NO_2 gas increased faster than NO gas during the process.

---

*Chemist, **Summer student, ***Manager, Canadian Explosives Research Laboratory, Mining Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

ÉTUDES PORTANT SUR LA STABILITÉ ET LA RÉACTIVITÉ DU NITRATE D'AMMONIUM
2ième PARTIE: DÉCOMPOSITION DU NITRATE D'AMMONIUM À L'ÉTAT SOLIDE

par

P.P. Lee*, K. Ketcheson** et R.R. Vandebeek***

RÉSUMÉ

On étudiera la décomposition thermique du nitrate d'ammonium (AN) sous son point de fusion à des températures constantes de 120°C, 140°C et 160°C et ce, dans deux systèmes différents. Le système statique, soit un environnement clos montra des résultats à la hausse, pour le pourcentage de perte de poids, la teneur en acide nitrique ainsi que les gaz nitreux, avec des températures plus élevées. On utilisa un système dynamique, alimenté d'un courant d'air, pour déterminer l'émanation de gaz durant la décomposition. La concentration de gaz NO_2 augmenta plus rapidement que celle de gas NO durant le processus.

---

*Chimiste, **étudiant, ***Gestionnaire, Laboratoire canadien de recherche sur les explosifs, Laboratoires de recherche minière, CANMET, Énergie, Mines et Ressources Canada, Ottawa.

CONTENTS

	Page
ABSTRACT	i
RÉSUMÉ	ii
INTRODUCTION	1
EXPERIMENTAL	2
Static System	2
Dynamic System	3
RESULTS AND DISCUSSION	4
Static System	4
Dynamic System	7
CONCLUSION	8
REFERENCES	9

TABLES

No.		
1.	Results of gas analysis using Draeger tubes	6
2	Concentrations of NO and NO_x gases at different temperatures, using chemiluminescent analyzer	7

FIGURES

No.		
1.	Schematic drawing of static system	11
2.	Schematic drawing of dynamic system	12
3.	% weight loss as a function of temperature	13
4.	% HNO_3 as a function of temperature	14
5.	pH as a function of temperature	15
6.	Thermal decomposition of ammonium nitrate, concentration of NO, NO_x as a function of time; chemiluminescent gas analyzer	16
7.	Thermal decomposition of ammonium nitrate in the presence of stainless steel at 160°C, concentration of NO, NO_x as a function of time; chemiluminescent gas analyzer	17

INTRODUCTION

Ammonium nitrate (AN) is a widely used ingredient of explosives. It has the advantage of appreciable chemical stability and low sensitivity to friction and shock. The disadvantage is that it is very hygroscopic.

AN is an inorganic salt which in its pure form has a melting point of 169.6°C. It has five different crystal forms depending on the temperature. The thermal decomposition above the melting point and phase transitions of the AN have been studied extensively [1-5]. All the investigators suggested that the decomposition of AN occurs by a series of consecutive reactions. Kolaczkowski et al. [6] suggested that at 165°C and above, the first stage is the endothermic dissociation of AN into nitric acid (HNO_3) and ammonia (NH_3). Both undergo exothermic changes in subsequent consecutive reactions. Feick and Hainer [4] suggested the following equations for AN decomposition.

at 170°C, $NH_4NO_3 \rightarrow NH_3 + HNO_3$ $\quad \Delta H = +148$ KJ/mole

at 290°C, $NH_4NO_3 \rightarrow N_2O + 2H_2O$ $\quad \Delta H = -69$ KJ/mole

Koper et al. [7] introduced the mechanism of gas phase reactions. The reaction paths are shown below:

$$HNO_3 \rightarrow OH^{\bullet} + NO_2^{\bullet}$$

$$NH_3 + NO_2^{\bullet} \rightarrow HONO + NH_2^{\bullet} \rightarrow NH_2NO + OH^{\bullet} \rightarrow N_2 + H_2O$$

$$NH_3 + OH^{\bullet} \rightarrow H_2O + NH_2^{\bullet} \xrightarrow{HNO_3} NH_2OH + NO_2^{\bullet} \rightarrow NH_3 + N_2 + H_2O$$

Findlay and Rosebourne [8] contributed information on the decomposition and stabilization of ammonium nitrate in the presence of oxidizable materials such as starch and woodmeal. The effect of nitric acid, ammonia, nitric oxide, nitrogen dioxide and other inhibitors on thermal decomposition of AN was also studied [6, 9-11].

Many studies have been done on this subject, however, there is insufficient knowledge of the mechanism of AN decomposition, especially at temperatures below the melting point. This lack of knowledge introduces difficulties in preventing fires and explosions during the production, storage

and transportation of AN. Therefore, studies into the thermal decomposition of AN below its melting point are important.

An accelerating rate calorimeter (ARC) was used for thermal stability evaluation of AN and ANFO [12]. It was also used for an accident investigation into an ammonium nitrate melt line explosion [13]. These applications provided some valuable information about the thermal properties of AN. Furthermore, the instrument is being used for studies of the thermal reactions of AN and metal powder. The instrument is able to detect exothermic reactions of AN with some metals at sufficiently low temperatures that thermal hazards are suggested [14]. Further understanding of the decomposition of AN at temperatures below the melting point could give some information on the mechanism of the reaction between AN and metals.

EXPERIMENTAL

STATIC SYSTEM

The experiments were designed to study the decomposition of AN aged at an isothermal temperature and in an enclosed environment. Ten gram samples of ammonium nitrate were weighed into a crucible using an analytical balance and were placed in a desiccator. The desiccator containing the sample was connected as shown in Fig. 1. The system was heated to the desired temperature in a temperature-controlled oven. A series of isothermal age decomposition studies were performed in duplicate at 120°C, 140°C and 160°C for 4 h and 20 h respectively.

After isothermal aging for the desired period of times, some analyses were carried out on the residue. Pure AN crystal without aging was used as a control.

(1) Weight loss

Weight loss was determined by weighing the crucible and sample before and after thermal aging.

(2) Nitric acid content

Nitric acid content was calculated from the titration data. A known quantity of AN sample was titrated with sodium hydroxide using methyl red as indicator [15].

(3) pH

An Accumet, model 520 digital pH meter was used. A pH 4.000 ± 0.02 buffer was used for calibration. Ten percent aqueous solution of the aged AN was prepared for pH determination at room temperature.

(4) Ultraviolet and Visible (UV-VIS) absorption spectroscopic analysis

A Shimadzu Double Beam Spectrophotometer, UV-200 was used for the analysis. The concentration of the solution was 0.2 g in 100 mL distilled water and was run against a reference of distilled water.

(5) Infrared (IR) spectroscopic analysis

The infrared spectrum of the aged AN was taken on a Perkin-Elmer 735B infrared spectrophotometer. Each sample was run as pellet in a KBr matrix at a concentration of 1-3%.

(6) Gas analysis for ammonia (NH_3) and nitrous fumes ($NO + NO_2$)

Draeger tubes were used to analyze the accumulated gaseous products. The tubes were used in conjunction with the Draeger gas detector pump to suck the air sample through the tube. When the gas was drawn through the Draeger tube, the concentration of the gas could be determined by the colour change of the indicating layer. The gaseous products were measured as parts per million (ppm).

DYNAMIC SYSTEM

The apparatus for the dynamic system consisted of a temperature-controlled oven, a gas chamber, and a chemiluminescent $NO-NO_x$ gas analyzer. The AN sample in the gas chamber was placed inside the oven which was heated to a preset temperature. One end of the gas chamber was connected to the chemiluminescent analyzer using Teflon tubing. The set up is shown in Fig. 2. Approximately 100 g ammonium nitrate was weighed accurately into the gas chamber and placed in an oven which was preheated to 100°C. The concentrations of NO and NO_x in the air sample were monitored at regular intervals. This procedure was repeated at temperatures of 120°C, 140°C and 160°C respectively. The quantity of NO and NO_x were measured throughout the test.

The chemiluminescent NO-NO_x analyzer works on the principal of light emission. When nitric oxide and ozone react in a reaction chamber, the following reaction occurs:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu$$

NO converts to NO_2 and the energy in the form of light is given off when the excited NO_2 molecules revert to their ground state. A photo-multiplier, sensitive to the resulting chemiluminescence, responds to the light in a narrow wavelength band which is unique to the reaction. The readings from the chemiluminescent response are linearly proportional to the concentration of NO. The NO_x concentration ($NO + NO_2$) is measured by converting the NO_2 to NO. In this case, the chemiluminescent response is linearly proportional to the total concentration of NO and NO_2 [16].

A study on the effect of stainless steel 304 on the thermal decomposition of AN was performed. Thirteen pieces of 1/2 in. long x 1/4 in. O.D. Type 304 stainless steel tubing, weighing approximately 28 g, were mixed into 100 g of AN in the gas chamber. The sample was placed in the isothermal environment at 160°C for a period of time. Evolution of NO and NO_x gases were measured using a chemiluminescent analyzer.

MATERIAL

Ammonium nitrate crystal, ACS grade, from Anachemia Chemical Ltd. was used.

RESULTS AND DISCUSSION

STATIC SYSTEM

It was noted during the course of the runs that the AN became solidified into a single mass and assumed the shape of the crucible. Also, a thin layer of white powder was found on the sides of the desiccator which indicated that sublimation had occurred. During the test, the oven temperature was controlled to ± 2°C. The results of analyses are discussed below.

(1) Weight loss

The weight loss was determined within 20-25 min after cooling to room temperature. The experiments were repeated a few times and the average percent weight loss was plotted as a function of temperature in Fig. 3.

(2) Nitric acid content

Nitric acid content in the aged AN was determined using a titration method. Pure fresh AN crystal was used as a standard and was found to contain 0.012% HNO_3. The average values of $\%HNO_3$ in the aged AN was calculated from several experiments and was plotted as a function of temperature in Fig. 4. It shows that HNO_3 in AN was higher after it was aged at higher temperature. However, the HNO_3 contents are similar after aging at 120°C and 140°C for 4 h.

(3) pH

pH of aged samples was measured as a 10% aqueous solution of the AN. The average values of the experiments were plotted against temperature as shown in Fig. 5. After aging at higher temperatures, the AN has lower pH values which agrees with the results of % HNO_3.

(4) UV-VIS absorption spectroscopic analysis

The spectra of aged and non-aged AN have maximum absorbance at 303 nm which is attributed to the nitrate ion. No other absorption peak was found. The absorption maximum of AN cited in the literature was compared to the experimental value [17].

(5) IR spectroscopic analysis

An IR spectrum of AN, aged at 160°C for 20 h, was taken and compared to the spectrum of a non-aged AN sample. No difference was detected in the spectra.

(6) Gas analysis for ammonia and nitrous fumes

Because the set up used a fixed volume container, vacuum was created in pumping air through the sampling tube after a few pumps of the Draeger sampling pump. As a result, the concentration of the gases determined may contain slight inaccuracies. The results are summarized in Table 1.

Table 1 - Results of gas analysis using Draeger tubes

Temperature	4 hours				20 hours			
	NH_3		$NO + NO_2$		NH_3		$NO + NO_2$	
(°C)	stroke	ppm	stroke	ppm	stroke	ppm	stroke	ppm
120	2	-	2	1.4	2	trace	2	3.0
140	3	trace	2	3.0	2	trace	2	5.1
160	3	3.5	2	6.0	2	-	2	8.3

Figure 3 demonstrates a drastic weight loss in AN aged at 160°C for 20 h. From the previous research, the rate of decomposition is promoted by the free nitric acid that is present. Nitric oxide and nitrogen dioxide also accelerate the decomposition process [9]. Figure 4 illustrates that the amount of HNO_3 increases greatly at 160°C. This sharp increase in free nitric acid could cause the high weight loss.

Figure 4, $\%HNO_3$ against temperature, indicates the $\%HNO_3$ content in the residue AN after heating at 120°C for 20 h is lower than the 4 h treatment, corresponding to a higher pH in Figure 5. The transition of this tendency occurs between 124°C to 128°C as shown in both figures. At 140°C and 160°C, the HNO_3 content increases rapidly after heating for 20 hours. The reason for this result could not be explained from these experiments.

As shown in Table 1, the AN aged at 160°C for 4 h has 6 ppm nitrous fumes and 3.5 ppm of NH_3. For the 20 h, 160°C aging experiments, the nitrous fumes were measured at the 8.3 ppm level but no NH_3 was detected. According to some investigators, ammonia has an inhibition effect on AN decomposition. Because no NH_3 was detected during the 20 h 160°C isothermal aging test, nitric acid could further enhance the decomposition process. The experimental evidence appears to support this explanation; a rapid rise in weight loss is due to the increase of nitric acid and the decrease of ammonia. The absence of NH_3 during the 160°C, 20 h aging test is caused by the reaction of NH_3 with $NO_2^{\bullet}$ radicals and produced the final products deduced by Koper [7].

DYNAMIC SYSTEM

An AN sample in the oven was step-heated from 100°C to 160°C in 20°C, steps. The temperature was allowed to equilibrate between each heat step. The gases NO and NO_x were analyzed during the test and the data are plotted as concentration against time in Figure 6. Sample size was 100 g and the flow rate of air through the sample was 57 L per hour. A few tests were performed and they had same gas generation patterns.

As demonstrated in Fig. 6, the concentration of NO gas increased very slowly from 100°C to 160°C. The concentration detected was in the 0.2 ppm to 1.3 ppm range. For NO_x gas, the sum of NO and NO_2 gases, the concentration increased sharply in the 160°C region. Average concentrations of NO and NO_x gases of several experiments at equilibrium temperatures are summarized in Table 2.

Table 2 - Concentrations of NO and NO_x gases at different temperatures, using chemiluminescent analyzer.

Temperature (°C)	Concentration (ppm) NO	NO_x
100	0.79	1.08
120	1.35	2.07
140	1.73	3.36
160 (at max. con.)	1.86	12.67

AN in the presence of Type 304 stainless steel tubing was isothermally aged at 160°C for a period of time. The effect of stainless steel on the decomposition of AN was studied by comparing the generation of NO and NO_x gases from the tests. The average maximum concentration of NO_x generated by pure AN decomposition was 12 ppm compared to 40 ppm NO_x generated by the AN with stainless steel present. Figure 7 is the plot of the data for the decomposition of AN in the presence of stainless steel at 160°C. NO has a maximum concentration of 2 ppm but NO_x has increased drastically in quantity. The presence of stainless steel appears to enhance the generation of NO_x gas,

but it does not demonstrate an abrupt increase in NO concentration. The higher concentration of gas evolved could be caused by a catalytic effect or the heat transferred faster and more uniformly in the presence of the SS tubing.

CONCLUSION

The static system illustrates an increase in weight loss and nitric acid content with an increase in temperature. The experimental data support the theory that HNO_3 accelerates the thermal decomposition of AN. The thermal aging at 160°C for 20 h shows diminishing NH_3 concentration which could indicate ammonia reacts further in a confined environment at elevated temperatures.

The results from the dynamic system indicate that the decomposition of AN is slow at a temperature below 140°C. However, there is a drastic increase of NO_x gas at 160°C. Then the concentration of NO_x decreases which correlates with a theory proposed by Koper that $NO_2^{\bullet}$ radicals react with NH_3 in the gas phase.

Further experiments are recommended on the analysis of the AN decomposition gaseous products. It is useful to analyze NH_3 concentration accurately using an infrared gas analyzer and NO, NO_x gases using the chemiluminescent analyzer simultaneously. The results may lead to a better explanation concerning the sharp rise of NO_x gas and the reduction of NH_3 gas in the present experiments.

REFERENCES

1. Sowell, R.R., Karnowsky, M.M., and Walters, L.C. "The transitions in phases II-III-IV in high purity ammonium nitrate"; J. of Thermal Analysis 3:119-129; 1971.

2. Choi, C.S., and Prask, H.J. "Phase transition in ammonium nitrate"; J. Appl. Cryst. 13:403-409; 1980.

3. Urbanski, "Chemistry and technology of explosives"; vol. 2; Pergamon press Ltd., Oxford; 1965.

4. Feick, G., and Hainer, R.M. "On the thermal decomposition of ammonium nitrate. Steady-state reaction temperatures and reaction rate"; J. Am. Chem. Soc. 76:5860-5863; 1954.

5. "The deflagration to detonation transition characteristics of molten ammonium nitrate, Part I"; Report of contracts, vol. 8; Mining Engineering, Queen's University, Kingston, Ontario.

6. Kolaczkowski, A., Biskupski, A., and Schroeder, J. "Effect of ammonia on the thermal decomposition of ammonia nitrate"; J. Chem. Tech. Biotechnol. 31:327-332; 1981.

7. Koper, J.H., Jansen, O.G., and Van den Berg, P.J. "A reaction mechanism for the decomposition of ammonium nitrate": Explosivstoffe, 8:181-183; 1970.

8. Findlay, A., and Rosebourne C. "Note on the decomposition and stabilization of ammonium nitrate in presence of oxidizable material"; J. Soc. Chem. Ind., 41:58-59; 1922.

9. Kolaczkowski, A., and Biskupski, A. "The effect of nitric oxide and nitrogen dioxide on the thermal decomposition of ammonium nitrate"; J. Chem. Tech. Bio-technol. 31:424-430; 1981.

10. Kolaczkowski, A., and Biskupski, A., "Nitric acid and ammonia concentrations as factors controlling the thermal decomposition of ammonium nitrate": Thermal Analysis, ICTA 80, 399-402.

11. Madany, G.H., and Burnet, G. "Inhibition of the thermal decomposition of ammonium nitrate"; J. Agr. Food. Chem. 16:1:136-141; 1968.

12. Lee, P.P., and Vandebeek, R.R. "Utilization of an accelerating rate calorimeter for the thermal decomposition studies of ammonium nitrate and ammonium nitrate-fuel oil explosives"; Division report MRP/MRL 83-35(TR) ; Energy, Mines and Resources Canada.

13. Lee. P.P., and Vandebeek, R.R. "Thermal stability evaluation of sample from ammonium nitrate melt line explosion by accelerating rate calorimetry"; Division report, ACEA/MRL 85-16 (TR); Energy, Mines and Resources Canada.

14. Lee, P.P., and Vandebeek, R.R. "Studies into the thermal stability and reactivity of ammonium nitrate. Part 1. The reactivity of various metal with ammonium nitrate studied by accelerating rate calorimetry"; Division Report, ACEA/MRL 86-29(TR); Energy, Mines and Resources Canada.

15. Fedoroff, B.T., and Sheffield, O.E. "Encyclopedia of Explosives and Related items"; vol 1; Picatinny Arsenal, Dover, New Jersey, U.S.A. 1960.

16. "Instruction Manual, Model 10AR chemiluminescent NO-NO_x gas analyzer" Thermal Electron Corporation, Massachusetts, U.S.A.

17. Jones, R.N. and Thorn, G.D. "Ultraviolet absorption of nitric acid solutions"; Canadian J. of Research. 27,B:580-588; 1949.

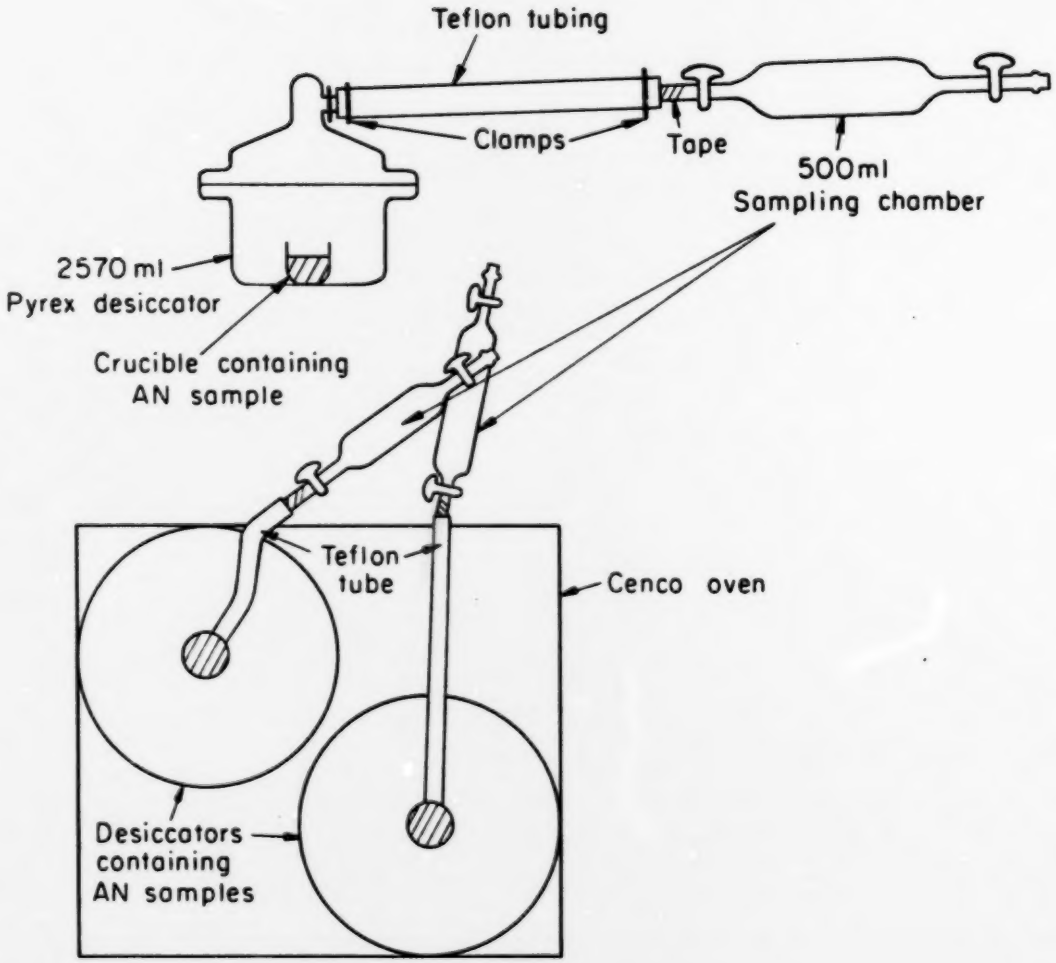

Fig. 1 - Schematic drawing of static system

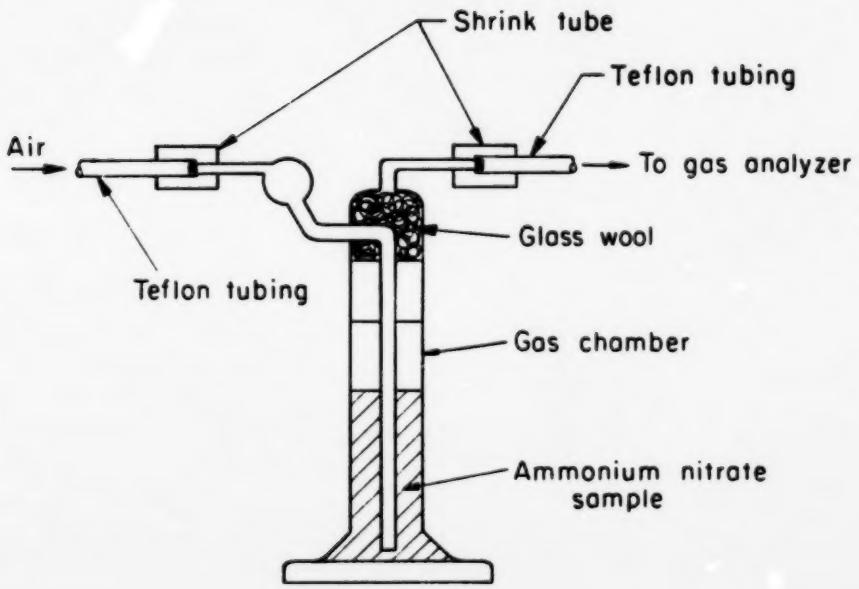

Fig. 2 - Schematic drawing of dynamic system

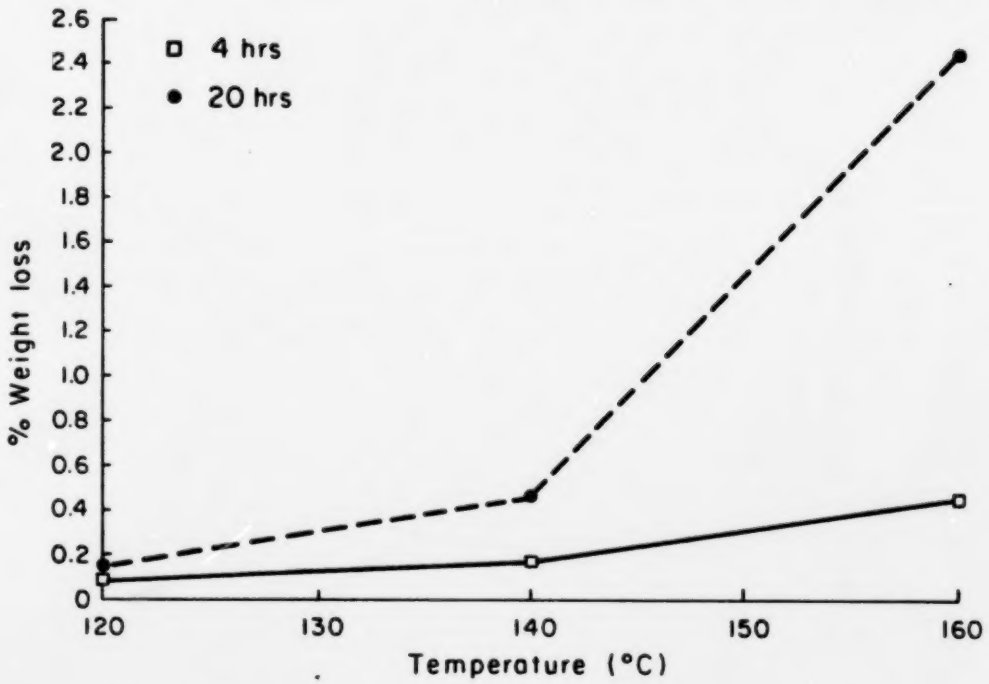

Fig. 3 - % weight loss as a function of temperature

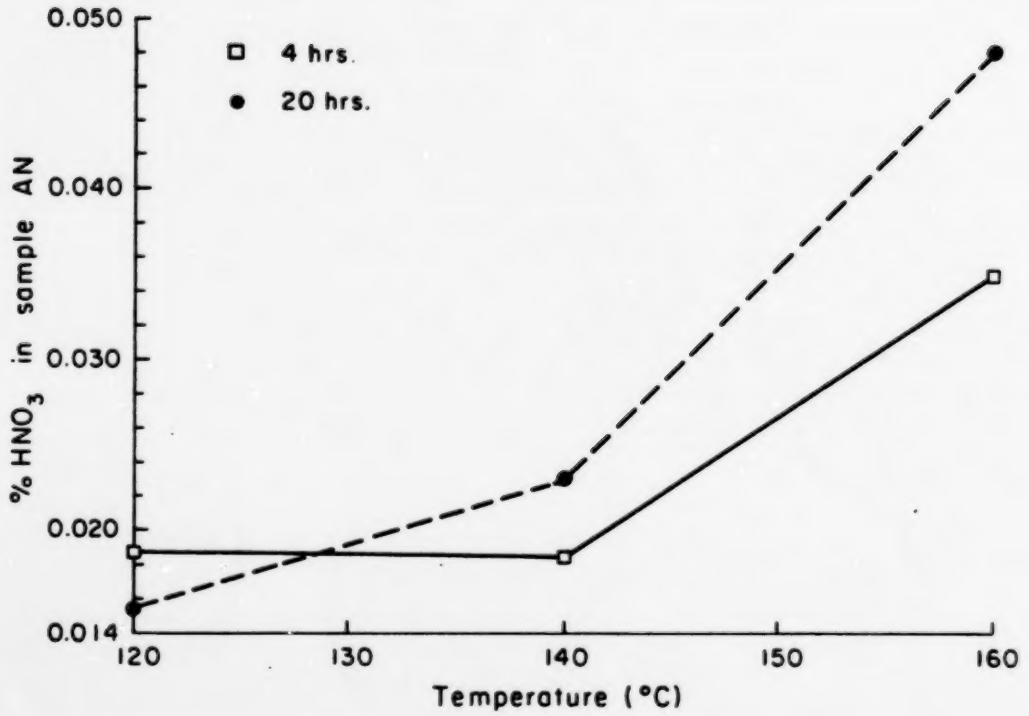

Fig. 4 - % HNO_3 as a function of temperature

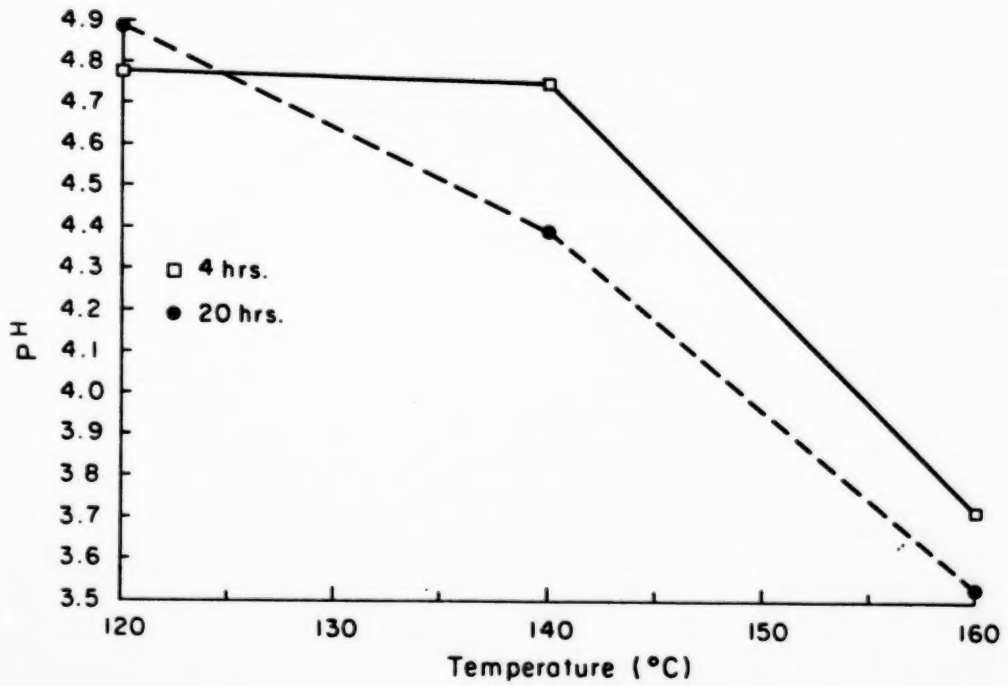

Fig. 5 - pH as a function of temperature

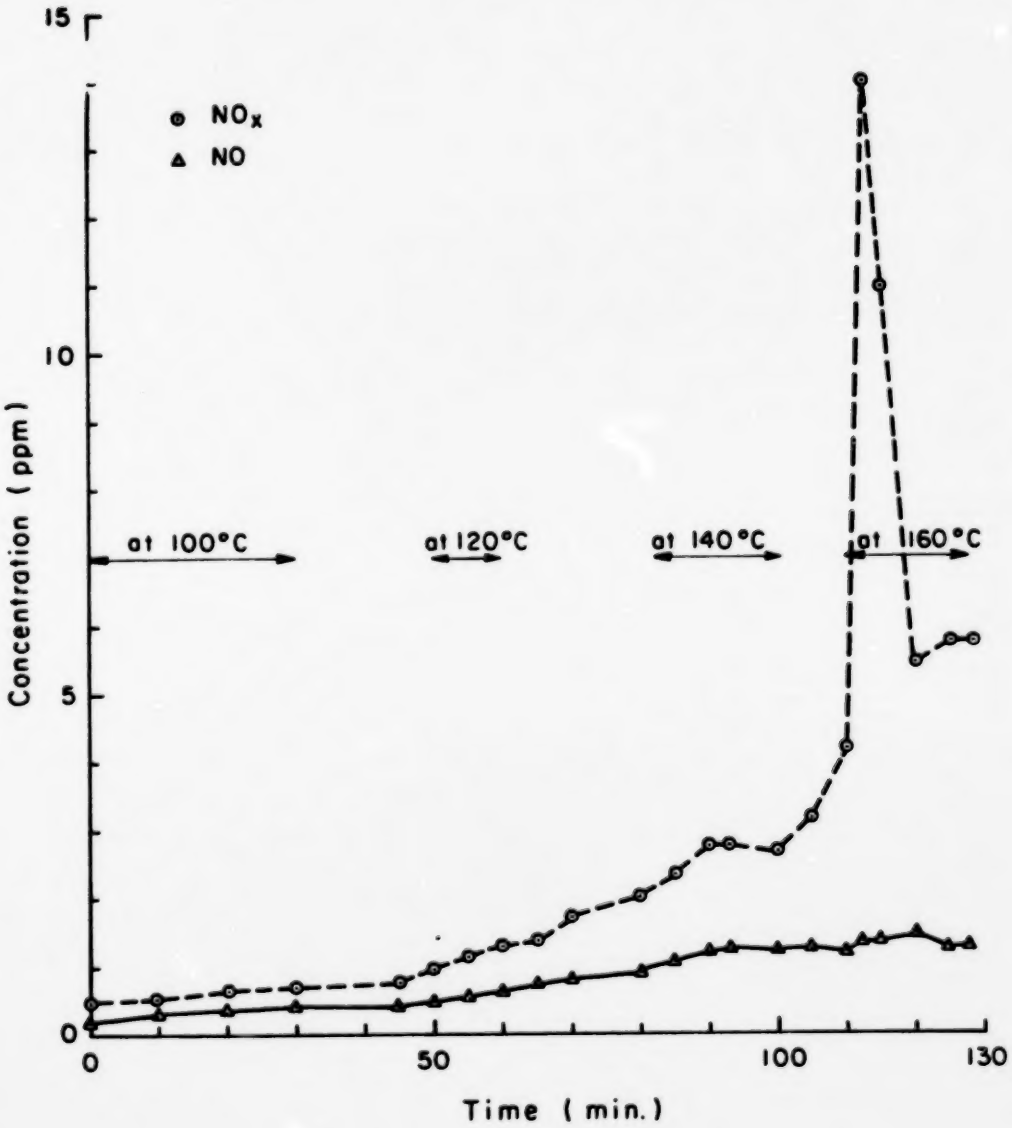

Fig. 6 - Thermal decomposition of ammonium nitrate, concentration of NO, NOx as a function of time; chemiluminescent gas analyzer

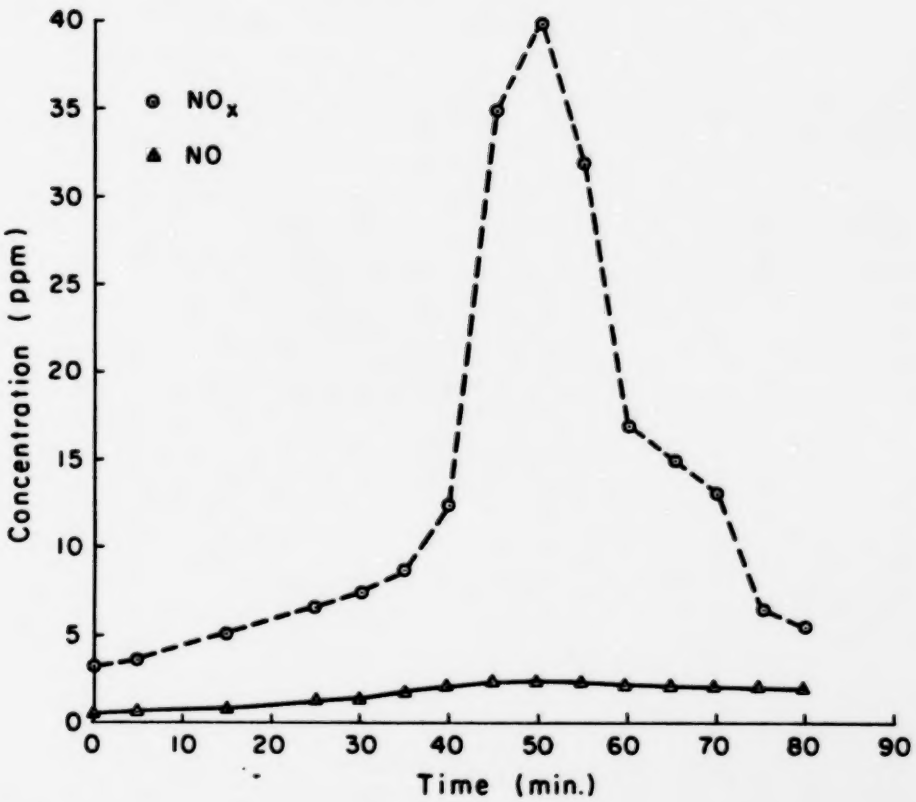

Fig. 7 - Thermal decomposition of ammonium nitrate in the presence of stainless steel at 160°C, concentration of NO, NOx as a function of time; chemiluminescent gas analyzer